Size effects in IR-optical properties of ultrathin Pb quantized films.

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Abstract. The reflectance difference (RD) as a function of film thickness was measured during Pb deposition on Si(111)-(6 × 6)Au surface at 105 K. The oblique incident *s*- and *p*-polarized light with energy range 0.25-0.60 eV was used. The component of the dielectric function tensor parallel to the surface was determined from the data of experiments and it oscillation due to quantum size effects (QSE) with period of 2 ML within the Pb monolayer-by-monolayer growth was observed.

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1. Introduction

It is well-known that optical and electrical properties of thin films behaive in an unusual way in contrast to physical properties of bulk materials. When the thickness of the smooth thin film become comparable to the de Broglie wavelenght of the electrons, more subtle effects, such as QSE can be detectible. A number of experimental works on low-energy electron reflection and transmission [1],[4],[5],[6],[7], electron tunneling [2],[3], electrical conductivity [8],[9],[10], valence band photoemission [11],[12], electron beam intensity [13], critical temperature [14],[15], Hall coefficient [16],[17], work function [18] measurements confirm earlier theoretical predictions [19],[20],[21],[22]. Influence of the QSE on growth morphology of Pb/Si(111) systems is the subject of the last investigation [23],[24],[25]. However, experimental evidence of the QSE in the optical properties of thin metallic films still is not so clear [26],[27],[28],[29],[30].

Theoretically, the influence of discrete quantum levels on the optical properties of the cubic particles has been analyzed by Wood and Ashcroft [31]. The formalism based on general random phase approximation (RPA) applied to simple particle-in-a-box model and a formula for dielectric constant of small metallic particle has been derived. The identity of the dielectric function of cubic particles and that of the film had been noted by Cini and Ascarelli [32]. In this paper, we study optical response

changes during epitaxial growth of ultrathin Pb films on Si(111)-(6×6)Au substrate by means of reflectance differential spectroscopy (RDS).

We used s- and p-polarized light with the incident photon energy range 0.25 - 0.6 eV. Clear evidence of QSE peaks with the period 2 ML of Pb film especially for small photon energies was observed. The experimental results were analyzed in the frame of the theory Dignam, Moskovitz and Stobie [33].

2. Experimental

The sample preparation and optical measurements were held in UHV chamber equipped with reflection high energy electron diffraction (RHEED). A gas-flow UHV liquid nitrogen cryostat and crystal quartz monitor were used for sample cooling and film thickness measurements during Pb films deposition process. The based pressure was less than 1×10^{-10} mbar.

A few direct current flashing was used to clear substrate and to produce Si(111)-(7×7) superstructure. In order to produce Si(111)-(6×6)Au reconstruction, about 1.2 ML of Au were deposited onto Si(111)-(7×7) and were annealed for 1 min at about 950 K with gradually lowering temperature to the initial state.

Optical system was consisted of globar, prism monochromator, polarizer and PbSe detector. Linearly polarized light was incident on a sample at oblique angle about 49°. A lock-in technique was used to recover reflected signal. Differential reflection spectroscopy based on measuring of a relative change in the sample reflectivity upon thin film deposition: $\Delta R/R = (R^{Pb+Si} - R^{Si})/R^{Si}$, where R^{Si} and R^{Pb+Si} are reflectivity of a bare substrate and a substrate covered with Pb atoms, respectively. The stability of the reflected signal $\Delta R/R$ during each measurements was better than 10^{-2}.

For better understanding of the growth mode of Pb and for controlling of the substrate quality RHEED technique had been used. RHEED oscillations were observed simultaneously with optical reflectivity experiments. The temperature of the sample during all time of Pb deposition was maintained at 105 K.

3. Results and discussion

3.1. Reflectance difference data measurements

Figure 1 presents RD data measured for s- i p-polarized light during Pb thin film deposition at 105 K onto a Si(111)-(6×6)Au substrate. The RD curve for energy $h\nu = 0.40$ eV increases with the thickness mostly linearly, while for the rest energies some unusual features are observed. This deviations from the linearity are more significant for smaller energies of the incident light. Experimental data also show different surface response depending on the type of polarization of the incident light. On the lower panel the RHEED beam intensity oscillations are presented, which indicates that films grew in the monolayer-by-monolayer mode [13]. The maximum of the RHEED intensity corresponds the situation when the layer is complete and surface is atomically smooth.

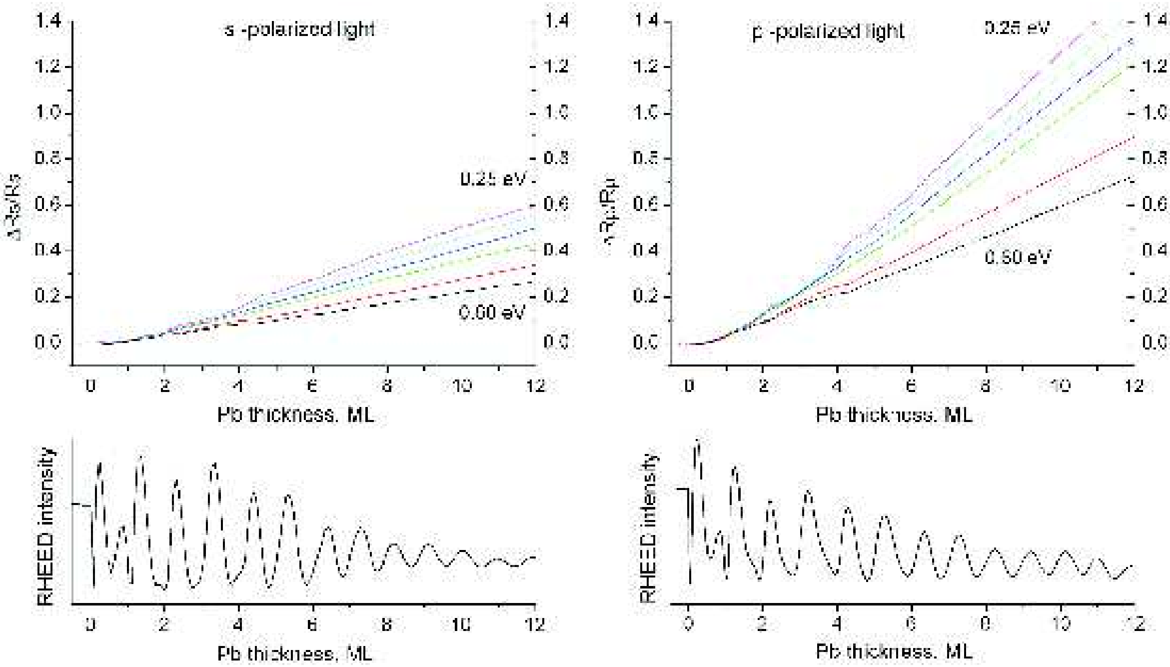

Figure 1. DR/R vs Pb film thickness for s-polarized light (left) and p-polarized light (right) with energies of incident light hν=0.25, 0.30, 0.35, 0.40, 0.50, 0.60 eV. Each curve was measured for a separately prepared thin film sample.

3.2. Imaginary part of the dielectric constant and quantum size effect

A few theoretical models have been proposed to describe changes in reflectance of the sample due to thin surface layer formation on the clear substrate. According to the classical McIntyre and Aspnes (MA) model [34], thin film as the homogeneous surface layer can be described by local and isotropic dielectric function. However, Feibelman have shown, that this model could not explain difference between s- and p-polarization spectrum of the free electron metal, due to the fact that the z − component of the electric field in the surface region has a strong frequency-dependence [35]. In the case of s-polarized light, electric field is parallel to the surface, varies slowly with going across it and no surface charge is induced. For p-polarization, the electric field component is normal to the surface, changes rapidly as one goes across the surface and can induce a surface charge which in turn can modify surface response. Since electric fields that are parallel and normal to the surface responds in the different way, it is necessary to describe the optical response introducing anisotropic dielectric tensor.

For this purposes we used a classical anisotropic layer Dignam, Moskovitz and Stobie (DMS) model [33], which assume uniform anisotropic surface layer to represent thin film on top of the isotropic substrate. The surface layer can be described by a complex local dielectric functions ε_z and ε_x as a components normal to and tangential to the surface plane. Rewriting equation for the relative reflectance changes $\Delta R/R$ of the DMS model in a more convenient way for the case of Pb thin film on Si substrate,

we get to the first order in terms d/λ:

$$\frac{\Delta R_\upsilon}{R_\upsilon} = \frac{8\pi d}{\lambda}\cos\theta\ \mathrm{Im}\left\{\left[\frac{\varepsilon_x^{Pb}-\varepsilon^{Si}}{1-\varepsilon^{Si}}\right]\left[1+\delta_{\upsilon,p}\frac{(1-(1/\varepsilon_z^{Pb})(\varepsilon_z^{Pb}-\varepsilon^{Si})/(\varepsilon_x^{Pb}-\varepsilon^{Si})}{(\cot^2\theta-1/\varepsilon^{Si})}\right]\right\} \quad (1)$$

where υ = p or s according to the type of polarization of the wave being considered, θ is the angle of incidence of the light beam, ε^{Si} - the complex bulk dielectric function of the Si substrate, $\delta_{\upsilon,p}$ is the Kroneker delta (equals 1 for $\upsilon = p$, 0 for $\upsilon \neq p$). On setting $\varepsilon_z^{Pb} = \varepsilon_x^{Pb} = \varepsilon^{film}$ equation (1) reduces to equations (24a) and (24b) of MA model.

Using equation (1) we calculate imaginary part of the dielectric function from experimental data presented on figure 1 both for s- and p-polarized light. For Si the bulk dielectric function after extrapolation to 0.25 eV is equal ε^{Si}=13+i0.001 [36]. We took Re$\{\varepsilon_z^{Pb}\}$=$Re\{\varepsilon_x^{Pb}\}$= –526 [37], but because of imaginary part of the substrate is close to zero, equation (1) is almost insensitive to the real part of the dielectric function of Pb.

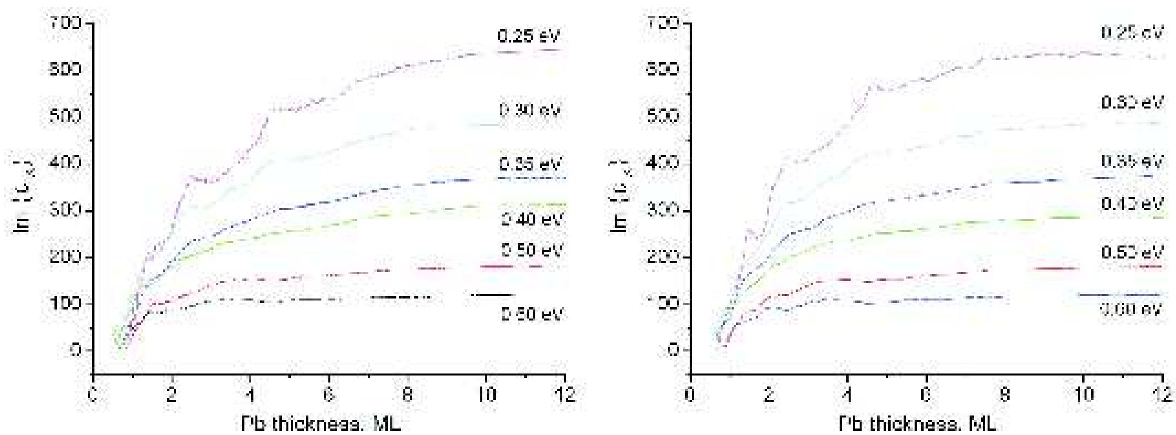

Figure 2. Imaginary part of the dielectric function parallel to the surface Im$\{\varepsilon_x\}$ calculated from experimental data of Fig.1 using equations (1) both for s- and p-polarization.

The results for Im$\{\varepsilon_x^{Pb}\}$ are shown in figure 2. The curve with energy 0.40 eV increase with minimal characteristic changes, but separates the other curves in to two parts. Several prominent features are observed: for the curves with small energies of the incident light $h\nu = 0.25 - 0.35$ eV a series of peaks with periodicity of 2 ML are clearly seen, for the curves with energies $h\nu = 0.50 - 0.60$ eV an equal number of dips with the same 2 ML periodicity and positions are also visible. These periodic oscillations of the Im$\{\varepsilon_x^{Pb}\}$ could be interpreted as the manifestation of the quantum size effect and are similar to the previously measured surface resistivity oscillations [10]. Since the positions of the peaks and dips are independent of the energy of incident light, we suppose that these variations are connected with free electron excitation and are caused by thickness dependent quantized conducting electron scattering. All curves saturates at 12 ML, with Im$\{\varepsilon_x^{Pb}\}$ that is typical to the bulk material. A peak near 1 ML originates

from the changes of the surface roughness induced by the quasi-monolayer by monolayer growth.

According to the quantum theory of Wood and Ashcroft [31], in which discrete energy spectrum of the electron has been taken into account, the imaginary part of the dielectric function of the thin metallic film with thickness d can be expressed as follows:

$$\mathrm{Im}\{\varepsilon(x)\} = \left(\frac{4}{\pi}\right)^4 \left(\frac{d}{a_0}\right) \frac{\Gamma}{x} \sum_{n=1}^{n_c} n^2(n_c^2 - n^2) \sum_{n'=1, n' \neq n}^{\infty} \frac{n'^{\,2}[\Delta^2 + (x^2 + \Gamma^2)][1 - (-1)^{n+n'}]}{\Delta^3[(\Delta^2 - x^2 + \Gamma^2)^2 + 4x^2\Gamma^2]} \quad (2)$$

where a_0 is the Bohr radius,

$x = 2\hbar\omega m_{eff} d^2/(\hbar^2\pi^2), \Gamma = (\hbar n_c^2/E_F\tau), n_c = Int\ (k_F d/\pi), \Delta = n'^2 - n^2$

E_F – is the Fermi energy, k_F – the Fermi wave number, τ – is the relaxation time ($\tau = l/v_F$), l – is the mean free path, v_F – is the velocity of the electrons on the Fermi level, m_{eff} – is the effective mass of the electron and the function Int takes the integer part of the argument. We calculate imaginary part of the dielectric function , using next experimentally obtained parameters of the Pb ultrathin films: $k_F = 1.6062\ \mathring{A}^{-1}$, $l = 20\ \mathring{A}$ and $m_{eff} = 1.002 m_e$ [12]. The results of calculations are shown in figure 3.

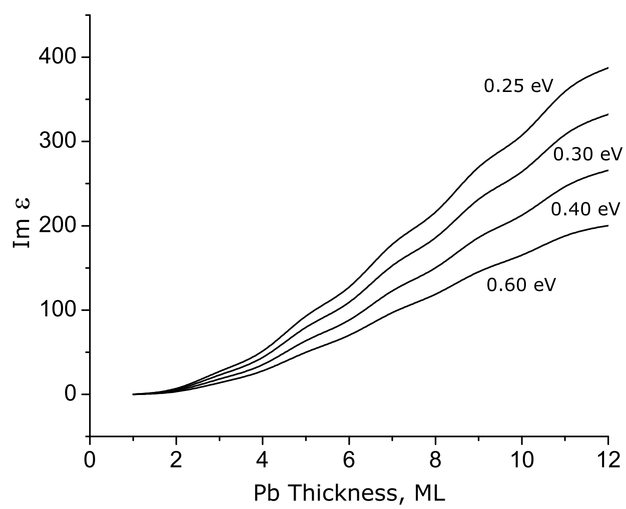

Figure 3. Imaginary part of the effective dielectric function calculated according to equation (2) for $k_F = 1.6062\mathring{A}^{-1}$, $l = 20\ \mathring{A}$ and $m_{eff} = 1.002 m_e$.

As it clearly seen $\mathrm{Im}\{\varepsilon\}$ growth vs thickness with periodic oscillations equal to 2 ML. Period of oscillation is independent of the incident light energy and agree with ones observed in experimental data. It is satisfy the QSE condition, when the film thickness d is equal to multiple of one-half the Fermi wavelength $\lambda_F/2$ [20], i.e. $Md_0 = N\lambda_F/2$, where M and N are integers. For Pb(111) this fulfilled with $(M, N) = (2, 3)$ [9].

3.3. Contribution of the electric field parallel and normal to the surface

Generally it is possible to extract $\mathrm{Im}\{\varepsilon_z^{Pb}\}$ knowing $\mathrm{Im}\{\varepsilon_x^{Pb}\}$ from measurements with s-polarized light, however in our experiments $\Delta R_s/R_s$ and $\Delta R_p/R_p$ were not measured simultaneously and the sample was changed during the time between experiments, so it is make problematic to find $\mathrm{Im}\{\varepsilon_z^{Pb}\}$ with adequate accuracy. In this case we take the bulk value of the dielectric constant for the energy $h\nu = 0.25$ eV equals $\mathrm{Im}\{\varepsilon_z^{Pb}\} = \mathrm{Im}\{\varepsilon_x^{Pb}\} = 645$ (figure 2), and define separately a contribution of $\mathrm{Im}\{\varepsilon_x^{Pb}\}$ and $\mathrm{Im}\{\varepsilon_z^{Pb}\}$ to differential reflectivity of p-polarized light rewriting equation (1) introducing $(\Delta R_p/R_p)_x$ and $(\Delta R_p/R_p)_z$ as follows:

$$\frac{\Delta R_p}{R_p} = \frac{8\pi d}{\lambda}\cos\theta\Big\{\mathrm{Im}\Big[\frac{(\varepsilon_x^{Pb}-\varepsilon_b^{Si})(\cot^2\theta - 1/\varepsilon_b^{Si}) + (\varepsilon_x^{Pb}-1)}{(1-\varepsilon_b^{Si})(\cot^2\theta - 1/\varepsilon_b^{Si})}\Big] + \\ + \mathrm{Im}\Big[\frac{\varepsilon_b^{Si}(1/\varepsilon_z^{Pb}-1)}{(1-\varepsilon_b^{Si})(\cot^2\theta - 1/\varepsilon_b^{Si})}\Big]\Big\} = \Big(\frac{\Delta R_p}{R_p}\Big)_x + \Big(\frac{\Delta R_p}{R_p}\Big)_z \quad (3)$$

where first term is the contribution of the surface response when electric field parallel to the surface, while the second one is the contribution of the electric field normal to the surface. Components $(\Delta R_p/R_p)_x$ and $(\Delta R_p/R_p)_z$ calculated from $\mathrm{Im}\{\varepsilon_x^{Pb}\}$ and

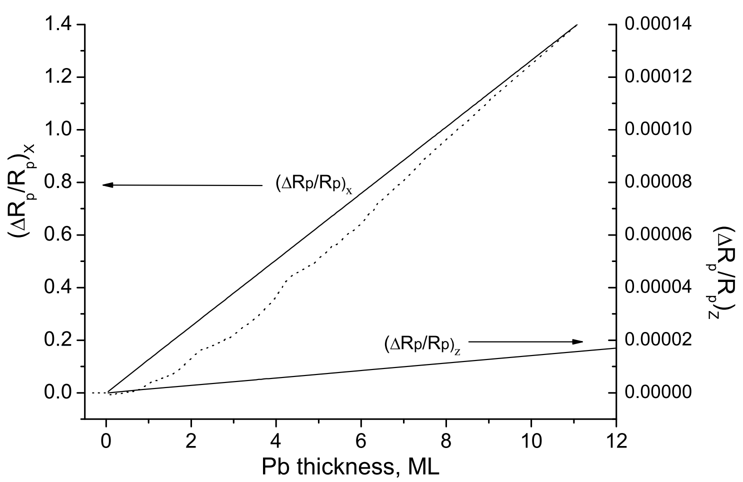

Figure 4. Calculated $(\Delta R_p/R_p)_x$ and $(\Delta R_p/R_p)_z$ dependences for photon energy $h\nu$=0.25 eV. Dashed curve represents $\Delta R_p/R_p$ measured during experiment with the same photon energy (figure 1).

$\mathrm{Im}\{\varepsilon_z^{Pb}\}$, respectively for incident photon energy $h\nu = 0.25$ eV are shown in figure 4. Scale of left axis is 10^4 times larger than the scale of the axis on the left side. As it clearly seen the main contribution to $\Delta R_p/R_p$ is due to the component parallel to the surface $(\Delta R_p/R_p)_x$, while the component perpendicular to the surface $(\Delta R_p/R_p)_z$ is close to zero. This is agree with the concept of the resistivity measurements, where momentum of conduction electrons is parallel to the surface of the film. The behavior

of the component normal to the surface is analogous to ones observed by Borensztein *et al* [38] during spectrum studies of the optical response of clean vicinal Si(001)(2×1) surface.

It is worth to note, that above mentioned models [33],[34], give the same $\mathrm{Im}\{\varepsilon_x\}$ dependence with the Pb thickness, calculated from the data obtained during experiments with the s- and p-polarized light. We have also analyzed $\Delta R/R$ using microscopic theory of Bagchi, Barrera and Rajagopal [39]. The results obtained in a long-wavelength approximation are similar to the results of DMS model for both polarization.

4. Conclusion

Optical reflectivity changes of Pb ultrathin films on the Si(111)-(6×6)Au substrate have been measured using reflectance difference spectroscopy both for s- and p-polarized light. Component of the imaginary part of the dielectric tensor parallel to the surface has been determined in frame of the classical Dignam, Moskovitz and Stobie model. It shows strong thickness dependence up to 10 ML with periodic oscillations equal 2 ML of Pb. These variations in optical properties of Pb thin fims are due to QSE and are correlated with electrical resistivity/conductivity oscillations. The contribution of the component of the imaginary part of the dielectric tensor perpendicular the surface into surface response is found to be close to zero in the studied film thickness and photon energy ranges.

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